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TRANSESTERIFICATION OF BEECHWOOD GLUCURONOXYLAN UNDER MICROWAVE IRRADIATION

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ABSTRACT: Xylan-type polysaccharides still represent a non-exploited renewable source of biopolymers available in huge amounts, applicable in native or modified form. Partially hydrofobized xylan derivatives represent important new biosurfactants [1]. An interesting alternative to the conventional hydrophobization methods, based on the esterification of polysaccharides with acid halides [2] and anhydrides represent the transesterification of xylans, CMS, CMC with methylesters of fatty acid [3,4,5]. Recently, a performing method by transesterification of carboxymethylcellulose under microwave heating has been reported [6]. The present work describes the transesterification of beechwood glucuronoxylan with methyl laurate microwave irradiation.The reaction was performed in DMF, or DMF/H_2O using microwave irradiation. The prepared xylan esters were characterized by FTIR spectroscopy and their surface-active and functional properties were tested.

KEY WORDS: glucuronoxylans, transesterification, microwave irradiation, surfactants, surface – active agent

1. INTRODUCTION

The last decade, polysaccharides have been recognized as raw materials in the detergent industry [7]. Polysaccharide-derived surfactants attracted increased attention due to their functionality as associative polymers, rheology modifiers and, more recently, also as body builder and co-surfactants in detergent formulations. These biopolymeric surfactants are of growing interest, because they are potential substitutes of petroleum-derived synthetic products, environmentally friendly, and show a higher compatibility with biological systems From the various reactions used for the hydrophobic modification of polysaccharides, esterification reactions have been the most investigated. The current trend is directed towards more efficient esterification methods in order to:

- avoid the use of harmful and toxic reagents, used in conventional syntheses
- minimise the application of organic solvents,
- optimise reaction conditions (lower the reaction temperature and dosage of acylation agents, shorten the reaction time, and increase the reaction efficiency).

Nowadays attention has been paid to apply the new heating system - microwave radiation also in the synthesis of polysaccharide esters. This is because of the reported various advantages of microwave heating in chemical reactions, when compared to classical heating [8]. As a continuation of the hydrophobic modification of xylans, we studied amphipnilic beechwood glucuronoxylan derivatives by transesterification reactions using methyl ester of lauric acid (ML) in dimethylformamide or dimethylsulfoxide as solvents:

$$\text{Xyl-OH} + \text{LaCOOCH}_3 \xrightarrow[\text{MW}]{\text{DMF or DMSO}} \text{LaCOOXyl} + \text{CH}_3\text{OH}$$

2. EXPERIMENTAL

2.1 Materials and analytical methods

Water-insoluble glucuronoxylan (**LX**) , a by-product of viscose production from beech sulfite pulp, was a gift from Lenzing AG (Austria):

Xyl = 92,5 % (of neutral sugars), MeGUA = 3,7 %, *Mw* ~ 5000 g/mol

N, N-dimethylformamide (DMF) was purchased from Lachema (Brno, Czech Republic), sodium dodecyl sulfate (SDS) was obtained from Sigma-Aldrich Chemie (Steinheim, Germany). Methyllaurate (ML) and Slovasol 245 were from VÚTCH-Chemitex s.r.o., Žilina, Slovakia.
The derivatives were characterized by FT-IR spectra (in KBr pellets, 2mg/200mg) obtained on the NICOLET Magna 750 spectrophotometer with a DTGS detector and OMNIC 3.2 software using 128 scans at a resolution of 4 cm^{-1}.

2.2 Transesterification of xylan (LX) with methyllaurate by microwave irradiation

In a typical experiment, the xylan sample (0.5 g) was suspended in DMF (15 ml) and then 1 g methyllaurate (ML) was added. The reaction mixture was stirred for 5 min in a laboratory minimixer at 20 000 rpm, followed by microwave heating for 1 - 5 min with microwave power 660 W. After reaction, the product was poured into 4-6 volumes of acetone and the precipitated derivative was separated by filtration, thoroughly washed with acetone, and extracted in a Soxhlet apparatus with acetone for 6 - 8 h.

2.3 Testing methods

The surface tension of aqueous solutions of the derivatives in the concentration range 0.1-5 $g.l^{-1}$ was measured at 25 °C using the Du Nouy ring apparatus [9]. The surface tension (γ_{min}) and critical micelle concentration (c.m.c.) were determined graphically as described in a previous paper [10]. The emulsifying efficiency was tested on 'oil in water' (**O/W**) type emulsions prepared by mixing 1 ml of paraffin oil dyed with Sudan IV and 9 ml of water containing 0.05 g of the xylan derivative in laboratory mixer (Heidolph DIAX 600) at 13 500 rpm for 1 min.
The stability of the emulsion was estimated at three different time intervals after the emulsions had been prepared, i.e. 5 min (h_1), 1 h (h_2) and 24 h (h_3), and expressed in terms of the height (mm) of oil and cream layers formed on the surface of the emulsion. The washing power (**WP**) of the derivatives at concentration 0.5 $kg.m^{-3}$ was determined by the method described more detailed in a previous paper [11] using cotton fabric (SK-standard 800 101) and model soil and washing time 10 min at 60°C. The antiredeposition efficiency (**ARE**) of the derivatives (c = 5 $g.l^{-1}$) was determined using standard cotton fabric (SK-standard 800 101) and model soil, and washing time 60 min at 50°C, as described in a previous paper [11].

3. RESULTS AND DISCUSSION

3.1 Preparation and characerization of xylan laurates

Due to the very low content of 4-O-methyl-D-glucuronic acid (MUA) side chains, LX was insoluble in water, giving dispersion of swollen particles in DMF and dissolved completely under these conditions in DMSO. The modification of LX by transesterification with ML was carried out in DMF or DMF/H_2O under homogenous and heterogeneous reaction conditions according to the method described for the modification of starch under microwave heating [12]. Method can obtained ester of xylan, when the carboxyl group of the MUA residues of the xylans is present in its ionized $-COO^-$ form, absorbing at ~ 1600 cm^{-1} and presence of ester is expressed at $\tilde{\nu}$(CO) ~ 1730 cm^{-1} (Fig. 1).

Prepared xylán esters at various reaction conditions, are summarized in Tab. 1. As seen in Tab. 1, the yield of the derivatives from LX xylan obtained by the reaction with ML varied between 0.,64 and 0,92 g/ 1g of initial xylan. The transesterification with ML gave lower yields due to the accompanying degradation of the xylan chains at the very high reaction temperature. However, important properties are the solubility and emulsifying efficiency of the derivatives that are essential attributes for their applicability as a polymeric surfactants. This first features are particularly important in the case of LX derivatives, as the starting xylan is insoluble in water. It gained solubility after introduction of the bulky hydrophobic substituents into the xylan chains. A similar phenomenon is known by the commercial water-soluble methylcellulose with low degree of substitution [13].

It can be explained by effect of the substituents to prohibit the re-aggregation and intermolecular hydrogen-bond formation of xylan chains during the recovery of the derivative from the reaction medium. Derivatives are partially soluble in water, but one of them is completely soluble in water (SR – 690). In comparison to derivatives SR-689 a SR-690 at uniform mass ratio and reaction time (Tab. 1) is important basic catalyst K_2CO_3. In the case, when catalyst was omitted, partially soluble derivatives were achieved. Transesterification in the presence of K_2CO_3 as catalyst in DMSO was water soluble derivative SR-690 achieved.

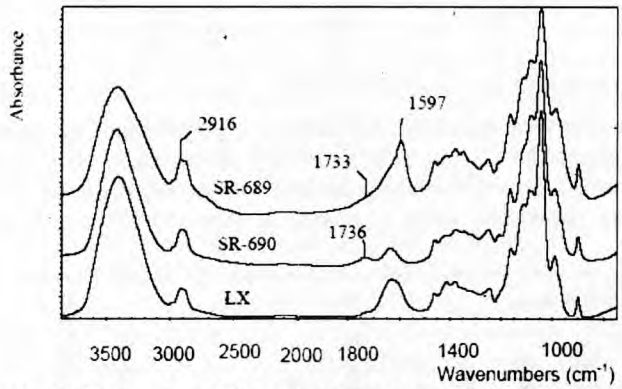

Fig. 1: FTIR spectra of the xylan laureates and started xylan LX.

Tab. 1: Reaction conditions by transesterification of xylan LX with with methyllaurate (ML) by microwave heating.

Sample	Solvent	LX : ML (Mass ratio)	Time (min.)	Temp. (□C)	Yield (g/1g)
SR – 674	DMF	1 : 1	1	130	0.64
SR – 678	DMF	1 : 1	3	140	0.78
SR – 682	DMF	1 : 1	5	140	0.81
SR – 676	DMF	1 : 2	1	130	0.69
SR – 672	DMF	1 : 2	3	130	0.73
SR – 680	DMF	1 : 3	3	141	0.74
SR - 686	DMF	1 : 3	5	143	0.77
SR - 685	DMF	1 : 4	5	143	0.85
SR – 687	DMF/H_2O	1 : 3	3	108	0.92
SR – 688	DMF/H_2O	1 : 4	3	109	0.84
SR – 689	DMSO	1 : 2	3	169	0.86
SR – 690	DMSO	1 : 2[a]	3	160	0.86

[a] with catalyst K_2CO_3

The stability of the emulsion was observed during 24 h measuring the height (mm) of the cream layer formed at the top the emulsion. As we can see in Tab. 2, derivatives have not emulsifying efficiency and some of the esters reduce the surface tension around 52 mN m^{-1}.

Tab. 2: Surface tension (γ_{min}), the critical micelle concentration (c.m.c) and emulsifying activity of xylan esters and controls.

Sample	Oil/cream layers (mm) [a]			γ_{min}	c.m.c
	h_1	h_2	h_3	(mN m^{-1})	(g l^{-1})
SR – 674	4/0	8/0	9/0	54,1	0.40
SR – 678	5/0	6/0	10/1	66,1	0.63
SR – 676	4/0	7/0	10/0	53,2	0.31
SR – 672	5/0	7/0	8/0	52,6	0.33
SR - 685	5/0	6/0	8/0	60,9	0.51
SR – 687	3/0	6/0	9/1	61,2	0.26
SR – 688	5/0	7/0	10/0	57,6	0,38
SR – 689	5/0	8/0	10/1	54,6	0,32
SR – 690	0/2	0/5	0/14	52,1	0,38
Tween 20	0/0	0/0	0/4	-	-
Slovasol 245	0/0	0/7	0/9	-	-

[a] formed after h_1: 5 min, h_2: 1 h, and h_2: 24 h

Some of the derivatives were tested for their detergent performance by washing power (WP) and antiredeposition efficiency (ARE) using SDS and CMC as standards. The results shown in Fig. 2 indicate that WP some of LX derivatives was good, and comparable to the standard SDS.
However, the ARE was rather low when compared to that of CMC, often used as co-builder in detergents [7].

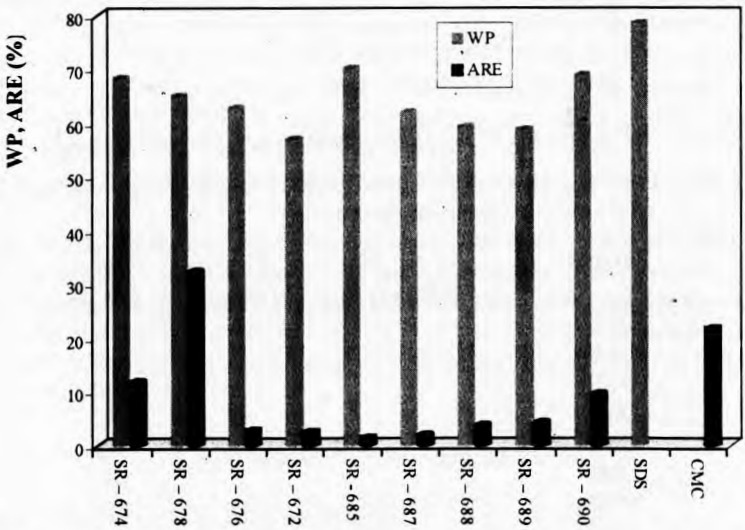

Fig. 2: *Performance properties of LX derivatives in comparison to controls SDS and CMC.*

4. CONCLUSION

Polymeric surfactants were prepared from glucuronoxylan by introduction of laurate substituents under homogeneous as well as heterogenous reaction conditions using transesterification method under microwave irradiation.

The water-solubility and tested functional properties were shown to depend not only on the extent of esterification, but also on the molecular properties of the starting xylan samples. Under suitable reaction conditions, partially soluble to water-soluble derivatives with acceptable surface-active properties can be prepared from water – insoluble glucuronoxylan preparations and might be useful as biosurfactants in various practical applications.

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5. REFERENCES

1 SKALKOVÁ, P., SROKOVÁ, I., SASINKOVÁ, V., EBRINGEROVÁ, A.: *Tenside Surf. Det.* **43** (3), 2006, 137-141.

2 SKALKOVÁ, P., SROKOVÁ, I., SASINKOVÁ, V., EBRINGEROVÁ, A., CSOMOROVÁ, K., JANIGOVÁ, I.: *Cellulose Chem. And Tech.* **40** (7) 2006.

3 RONEY, M.L.: *Polymer* **17**, 1976, 555 - 558.

4 GIRARDEAU, S., ABURTO, J., VACA-GARCIA, C., ALRIC, I., BORREDON, E.: IV European Symp. In Industrial Crops and products, Book of Abstr., Bonn, 1999, 129.

5 ABURTO, J., ALRIC, I., BORREDON, E.: *Starch/Stärke* **57**, 2005, 145 – 152.

6 TOMANOVÁ, V., PIELICHOWSKI, K., SROKOVÁ, I., ŽOLDÁKOVÁ, A., POLACZEK, J., PIELICHOWSKI, J.: *2nd International seminar Kraków, Vol. 2, 23-25 March 2006*

7 PAIK, Y. H., SWIFT G.: *Chem.Ind.*, **2,** 1995, 55.

8 CORSARO, A., CHIACCHIO, U., PISTARÁ, V., ROMEO, G.: *Curr. Org. Chem.* **8** 2004, 511.

9 LUKENHEIMER, K., MILLER, R.: *Tenside Det.* **16** , 1979, 312.

10 SROKOVÁ, I., EBRINGEROVÁ, A., HEINZE, TH.: *Tenside Surf. Det.* **38** , 2001, 277.

11 SROKOVÁ, I., MINÍKOVÁ, S., EBRINGEROVÁ, A., SASINKOVÁ, V., HEINZE, TH.: *Tenside Surf. Det.* **40** , 2003, 73.

12 GOURSON, C., BENHADDOU, R., GRANTED, R., KRAUSZ, P., SAULNIER, L., THIBAULT, J. F.: *Macromol. Chem.* **4** , 1999, 75 – 78.

13 CROON, I., MANLEY, E.: *Carbohydr. Chem.* **3** , 1963, 271.